

In connexion with my present line of work I have had to return to the spectrum of hydrogen, and I have photographed it, using an end-on tube, which I owe to the kindness of Dr. Monkhoven, whose device it is.* In the spectrum of the Monkhoven tube h is very well seen, though not so strong as the line near G.

What I wish, however, to draw special attention to now, is the fact that other lines more refrangible are seen; in the photographs I have obtained, one of them, within the limits of dispersion that I have employed (one dense prism of 60° , collimator 18 inches, and a small Dalmeyer rectilinear lens in the camera), is coincident with a line observed in the spectrum of calcium at λ 3968.0 (H).

More photographs are required to enable me to give the approximate positions of the other lines more refrangible.

VI. "On the Capillary Electroscope." By G. GORE, LL.D., F.R.S. Received December 6, 1879.

The following research was commenced with the hope of being able to make an exact measuring instrument of a modified form which I had devised (see page 37) of the "Capillary Electroscope," and to employ it for the determination of the different degrees of electromotive force of different metals in forming tables of electro-chemical series, with different electrolytic solutions.† With this object in view, I constructed and tried a considerable number of forms of the instrument; and employed a number of liquids, acid, neutral, and alkaline, as conducting media between the mercurial electrodes. In every case, however, an obstacle to uniform and accurate measurement sooner or later arose, viz., unequal adhesion of the mercury to different parts of the capillary tube.

It has been noticed by other investigators that the motion of the slender column of mercury in Lippmann's "Capillary Electrometer" suddenly stops whilst under the electric influence, and this has been supposed to increase the value of the instrument by rendering its indications sensibly instantaneous. According to Lippmann also "when the circuit was closed" by a metallic conductor, "all irregularities at once disappeared" ("Phil. Mag.," April, 1874, p. 284). This sudden stoppage of the mercury, however, whilst under the influence of the current is, I believe, in every case due to a sudden increase of mechanical resistance, usually caused by unequal adhesion

* It is right to add, however, that this form of tube also suggested itself to Professor Piazzi Smyth quite independently.

† See "On the Chemico-Electric Relations of Metals in Solutions of Salts of Potassium."

of the mercury to different parts of the tube, but sometimes by a minute trace of solid substance in the tube. With a very feeble current this adhesion shows itself in several ways, usually by a more or less sudden retardation or stoppage of the motion of the mercurial column, by a delay in its commencement of motion, or by its non-movement. The current I have employed has, in nearly all cases, been a very feeble one, obtained from two wires, one of copper, and the other of platinum, each about 1 millim. diameter, immersed about 2 or 3 millims. deep in common drinking water. With a very sensitive instrument, and a capillary tube as free from obstruction as could be obtained, this power has been sufficient to move the meniscus 10 or 20 millims.

A common cause of obstruction consists of impurities (especially oxide) in the mercury; the metal therefore should be as pure as possible. I have obtained it sufficiently pure by distilling the ordinary metal twice, then shaking it violently with dilute nitric acid, washing it with distilled water, shaking it again strongly with a dilute solution of potassic cyanide (which very effectually removes oxide), washing it again, and filtering it through a minute hole in the point of a paper funnel. The mercury should be kept in a closed bottle, and be frequently filtered to remove dust from its surface whilst being used, because the most minute speck of solid matter, even that which is invisible to the unassisted eye, is sufficient to stop the capillary tube. The solution also should be kept perfectly clear by means of filtration. Another cause of stoppage is the employment of glass tubing into which dust has been allowed to enter; this may be obviated by employing newly-made tubing, sealed at its ends by wax; with such tubing I have obtained no manifest advantage by washing it with acids, alkalies, ether, &c., nor by allowing a stream of clean mercury to run through it. After having taken all these precautions, there remains a very common cause of stoppage of the motion of the mercury, viz., portions of air or gas adhering to the tube; these consist either of minute films of air, or if the current is too strong, also bubbles of gas liberated from the electrolyte.

One of the most effectual modes of removing the air or gas is to repeatedly cause by mechanical means (such as compression of the pressure-chamber, or by change of position of the instrument from horizontal to vertical and *vice versâ*) the mercury and conducting solution to move freely to and fro through the whole of the fine part of the tube whilst the circuit is closed, and expelling occasionally a few drops of mercury from the end of the tube; employing also an electric current in a suitable direction to assist the motion. If there remain any adhering portions which are not removable by these means, diminished pressure, combined with an electric current from the point of the capillary towards its larger part, and the simultaneous

application of a hot plate of metal to the locality of the adhesion, rarely fails to remove them. Notwithstanding, however, all these precautions, the meniscus often subsequently sticks at a particular place without any apparent cause, and without the presence of any body visible by the aid of a microscope magnifying from 30 to 50 diameters. Free use of the instrument reduces many of these adhesions; it also gives rise to fresh ones. Immovable adhesions of the mercury frequently occur, or are subsequently produced by use of the instrument which interfere with the accurate measurement of so feeble an electric power as that mentioned above, and appear to be due to irregularities of smoothness in the glass itself; the best precaution to take in such cases consists in selecting as the sphere of the movement of the meniscus a portion of the capillary tube known to be free from such a source of error; but even such a space does not permanently remain free.

By employing a suitable tube, dilute sulphuric acid as the liquid, and taking all the above precautions, I have constantly found that the mercurial column, instead of moving from point to point with a jerk and stopping suddenly, moved with a gradually diminishing speed until it stopped. The momentary movement and sudden stoppage occurs more readily with a short capillary tube and currents of greater power than that above mentioned, but with a long tube, as free as obtainable from irregular adhesion, a movement of from 10 to 20 millims. not unfrequently occurs, requiring in some cases as much as 80 millims. variation of height of mercury pressure to bring the meniscus back to its original point. If the tube happens to be one of parallel bore, and especially if its lower part enlarges towards its lower extremity, such a current as the one mentioned will cause the meniscus to descend as much even as 5 or 6 centims., and the mercury to run out at the end of the tube. The influence of gravity no doubt operates in all these cases, but with the same electric power, and whilst using a tube the diameter of which does not diminish too rapidly towards its point, the column usually moves more readily towards the end of the capillary than the reverse, whether the instrument be in a vertical or horizontal position. The mercury in all cases tends also to pass from the form of a cylinder to that of a sphere, and if it once gets beyond the end of the tube, it forms a globule which draws the narrower part rapidly into itself by its great cohesion. Similarly if the tube is too taper the mercury tends to draw itself upwards towards the wider cavity.

A good capillary tube is essential; the only way I know of obtaining it is to make a number of tubes and try them until a suitable one is found. Glass tubing, of an external diameter of about 6 to 8 millims., and having a bore of about one-third or one-fourth of a millimetre, is of a very convenient size for making the capillary, because

it may be drawn out to a sufficient degree of fineness at one heating; that having a circular bore it is less likely to become clogged by use than that which is oval; and it is an advantage to employ that which has white enamel at the back. Success in making the capillary depends largely upon careful manipulation and the employment of a flame of suitable size; I have used a Bunsen flame about an inch in height and half an inch in diameter, for drawing long capillaries by a single heating, or a very minute flame of a small spirit-lamp for drawing out a short one by a second heating. Within certain limits, I have found that the finer the capillary tube the greater is the movement in it of the meniscus by a given electromotive force, and the greater the pressure required to balance that force; but if the bore of the tube be extremely fine, say $\cdot 01$ millim., the instrument becomes less sensitive, probably owing to increased adhesion or to increased conduction-resistance of the minute column of solution. A convenient bore is about $\cdot 03$ to $\cdot 04$ millim., and an external diameter of $\cdot 3$ to $\cdot 4$ millim. Under uniform pressure, the meniscus moves not only through a much greater length, but also at a much faster rate, in the finer portion of a tube of moderate diameter, than it does in the coarser part, and this occurs even in tubes the internal diameter of which diminishes to their very extremity. Tubes of parallel bore are not usually suitable for the instrument (especially if the latter is used in a vertical position), because, instead of presenting a resistance gradually increasing downwards, as they should do, they offer the reverse. The best form of capillary is one which becomes narrower at a sufficiently increasing degree towards its free end. I have employed capillaries varying in length from 5 to 15 centims. with equal advantage.

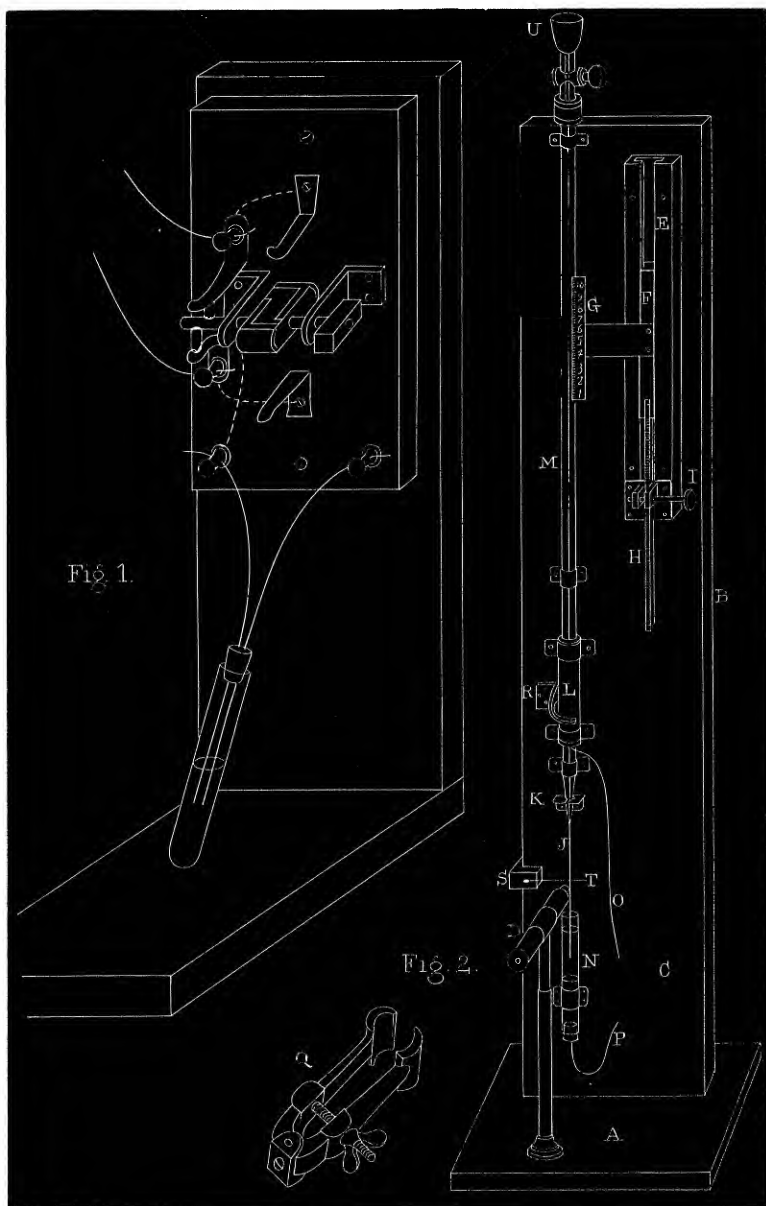
Considerable pressure is often requisite for filling the capillary tube, and for overcoming obstructions; to produce it, a compressible pressure-chamber is much more convenient than a tall column of mercury. An excellent chamber may be formed of a piece of vulcanized india-rubber tubing, about 6 or 8 centims. long, 3 millims. bore, and 15 millims. external diameter, such as is employed as "engine-packing." It is more convenient to have the platinum wire (for connexion with the column of mercury) inserted through the side of this tube than through that of the glass one, because the former does not so readily cause the wire to be broken. To insert the wire, one end of the tube is stretched open by means of a small pair of pliers; a needle, wet with glycerine, is then forced very obliquely through the india-rubber close to the end of the tube, and after its removal a fine wire may be readily forced through the minute stretched hole and the pliers then withdrawn. After the capillary tube has been fixed in this chamber (which must be previously made scrupulously clean), the end of the chamber adjacent to the terminal and capillary must be securely bound round

with wire to prevent leakage. As it often requires considerable pressure to force the mercury through the tube, especially when there exists both a mechanical obstacle and a stoppage of the electric current, a strong pressure screw, with its clamp capable of grasping at least an inch in length of the chamber, is absolutely necessary.

I have tried several plans of mechanically compensating the electro-capillary effect, the most convenient of which is to surmount the pressure-chamber by a vertical glass tube about 30 or 40 centims. high, and 1 millim. bore, with its lower end opening into the chamber, and its upper end also open, but capable of being closed by means of a glass cock, having an open cup at its upper extremity. This arrangement admits of great pressure being applied to the chamber, by means of the screw and clamp, and also of crudely measuring in millimetres height of mercury the compensating pressure necessary to depress the mercury to the neutral point whilst the current is passing. This upper tube also, like the capillary one, has the disadvantage of offering unequal resistance to the passage of the mercury by unequal adhesion, so that a small movement of the screw of the pressure-chamber is not often at once attended by a simultaneous movement of the mercury at the top and bottom of the column.

The voltaic current was very conveniently manipulated by the aid of a small moveable apparatus, so constructed that by turning its handle the first quarter of a revolution, the two wires of the electro-scope were connected metallically together, and the current insulated from them; by turning it a second quarter, the current was sent in one direction through the electroscope; by turning it a third, the wires of the electroscope were disconnected and perfectly insulated (the base of the instrument being of ebonite); and by turning it the fourth quarter, the current was sent through the electroscope in a reverse direction. This apparatus may be easily made by prolonging the axis of a common electric reverser, fixing two projecting metal studs on opposite sides of the prolonged part (*but not opposite to each other*), and attaching two vertical springs to two binding-screws fixed on the base, so that when the studs pressed against the upper ends of these springs, the circuit was closed between the ends of the wires attached to the two electrodes.

In the engraving, fig. 1 represents the reverser fixed vertically to a moveable wooden stand. The dotted lines show the directions of four connecting wires at the back of the ebonite base of the instrument. The wires from the voltaic cell are attached to two binding-screws, which are connected with the two metal standards that support the moveable axis. The terminal wires of the electroscope are attached by means of binding screws to two vertical brass springs, so fixed as to press against the two metal studs projecting at right angles from the moveable axis; the terminals are also further con-



nected, by means of the wires beneath the base, with the two other and ordinary vertical springs of the instrument, so that by turning the handle they may be disconnected from the studs and connected with those springs, and through them, the axis and standards, with the voltaic cell, and receive a current in either direction, according to the position of the handle. The sketch represents the handle and axis in the above-mentioned first position, with the two wires of the electroscope metallically connected together, but insulated from the cell.

The usual form of the electroscope I have employed is represented in fig. 2. A is a wooden base, B a wooden upright board fixed to it. C is the situation of the reverser. D a microscope, capable of vertical and horizontal movement, having a magnifying power of about 30 to 50 diameters, and provided with a "spider-line." E is a grooved piece of wood fixed to the upright stand. F a wooden slide, with a moveable scale, G, worked by a metal rack H, and pinion with handle, I. J is the capillary, supported by a perforated little brass shelf, K. L is the pressure-chamber. M the glass tube containing the compensating column of mercury. N a thin glass tube, about 5 millims. bore, containing the mercury and conducting solution. O and P are the terminal platinum wires for attachment to the screws of the reverser. Q is a strong clip, shown separate from the instrument. R is a metal support for the clip. S is a moveable slide of cork, carrying a very fine hair, T, for indicating the position of the meniscus. It is not usually necessary to measure the amount of movement of the meniscus. Some cotton wool is placed in the cup, U, and the cup is covered with a lid to exclude dust. A strip of white paper is affixed behind the capillary portion of the tube to form a white background, and the instrument requires to be used in a good light.

Having found by additional experiments that in certain cases the mercury moves in an opposite direction to the electric current, I am now engaged in examining that fact, and in completing an investigation of the causes and conditions of the movements.

VII. "Chemico-Electric Relations of Metals in Solutions of Salts of Potassium." By G. GORE, LL.D., F.R.S. Received December 8, 1879.

The following experiments were made with the object of determining the chemico-electric positions of various metals, &c., in solutions of salts of potassium of various strengths, and at different temperatures; and also with the intention of ascertaining, by the aid of Lippmann's



Fig. 1.



Fig. 2.

